Detonation Spin in Driven Shock Waves in a Dilute Exothermic Mixture

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There have been many uses of shock waves in diluted mixtures of exothermic reactants for studies of chemical reaction rates. It was once commonly thought, for lack of evidence to the contrary, that one could operate in a regime free of complications from spontaneous "detonation" phenomena arising from the deposition of the reaction energy in the flowing gas by generating shock waves faster and stronger than the Chapman-Jouguet wave for the dilute mixture. Such shock waves are in reality overdriven detonation waves, and the only basis for distinguishing them from strong detonation waves in more concentrated mixtures is the fact that the dilute mixtures, if not supported, may fail to sustain a slower, Chapman-Jouguet velocity wave. This distinction is one of degree rather than of kind, and recent experience with unsupported detonations and overdriven detonations in detonable gas mixtures indicates that three-dimensional structure which characterizes the Chapman-Jouguet velocity waves remains present, on a progressively finer scale, in overdriven waves.[1,2]

The occurrence of transverse waves or other instabilities in driven shock waves in dilute, only mildly exothermic mixtures has been less completely characterized. Indeed, many successful investigations of kinetics of exothermic reactions have been carried out in shock waves in dilute mixtures without major or even noticeable interference. On the other hand, there have been isolated reports of "instabilities", in the reaction zones in particular, under circumstances where the system was diluted well beyond the limit of detonability and the shock wave was clearly stronger than a Chapman-Jouguet wave. Examples of these occurrences may be found in studies of the hydrogen - bromine reaction,[3] ozone decomposition,[4] and hydrogen-oxygen combustion.[5] The present paper reports the occurrence of such instabilities in shock waves in a mixture of 1% C_2H_2, 1.5% O_2, 97.5% Ar and the identification of conditions where the phenomena exhibit the recognizable and quasi-reproducible form of single-headed spin.[6,7]

Experimental

The experiments reported here were carried out in the 10 cm i.d. circular brass shock tube used for several previously reported chemical investigations.[5] Several different test section configurations were utilized for the various kinds of diagnostic experiments. Either brass shim stock or Mylar sheet diaphragms were used, and the driver gas was hydrogen. The several batches of 1.0% C_2H_2, 1.5% O_2, 97.5% Ar test gas mixture were prepared manometrically from tank argon and a single, homogeneous stock mixture of 40% C_2H_2, 60% O_2 prepared initially from tank supplies. The composition of one batch was checked by mass spectral analysis, and 0.03% N_2 was the only detected departure from the intended composition. Experiments were carried out at initial shock tube pressures, p_0, of 20, 50, and 120 Torr.

Shock wave speeds were monitored by raster oscilloscope recording of the progress of the shock front past five piezoelectric pressure transducers spaced at 30 cm or longer intervals along a 140 cm or longer segment of the tube beginning 200 cm or 350 cm from the diaphragm.

In other experiments, where the departure of the shock front from planarity was under examination, four of the piezoelectric gauges were arranged at 90° intervals around the tube perimeter in a plane perpendicular to the axis, and their responses were displayed on four synchronized oscilloscope traces.

The presence of OH radicals in the combustion zone was monitored in many of the experiments by oscilloscope recording of the absorption of a beam of ultraviolet

OH molecular line radiation[9] which passed diametrically across the tube through quartz windows.

Mylar foils coated with wood smoke soot[2] were placed against the interior surface of the shock tube end flange in many of the experiments to record the presence of irregularities in the shock front reaching the tube end. Smoked foils lining the side walls along a 14 cm length of the test section were also used in sone experiments. The loci at the tube wall of the abrupt intersections of segments of creased shock waves are recorded as inscriptions in the soot coating.

Finally, open shutter photography in a 60 cm long glass extension of the test section was used to record the luminous trajectory of the spinning reaction zone - shock front complex in shock waves exhibiting the single-headed spin phenomenon.

Results

The initial results which suggested that spin-like irregularities might be present in promptly reactive shock waves in the 97.5% Ar mixture consisted of the occurrence of quasi-periodic undulations in spectrophotometric records of OH radical concentration in the reaction zone, which persisted for several hundred microseconds after passage of the shock wave. These records did not identify the instability definitively, nor have they proven to be even reliable indicators of the presence of instability in all instances. Accordingly, the investigation of the instability phenomena turned to the inclusion of other diagnostic techniques with which we have experience from the study of gaseous detonations.[2,6]

Positive confirmation of the occurrence of single-headed spin was made with a smoked foil along the inside wall of the tube. After passage of a spinning wave, the smoke layer bears a helical, ribbon-like inscription. The forward edge of the ribbon is the path of the backward pointing crease in the otherwise convex shock front. The trailing edge is the path of the rear terminus of the transverse detonation wave which propagates in the compressed, unreacted gas accumulated behind the weaker region of the primary shock front. This promptly reactive transverse compressional wave couples the revolving crease in the primary shock front to the predominantly circumferential acoustic oscillation of the pressure of the column of burned gas flowing behind the combustion wave system. The phase of the helix in the tube and also the pitch angle, Θ, whose tangent is the ratio of the axial to the circumferential velocity component, is recorded by the side wall smoked foil. Good specimens of these single spin records were obtained at initial pressures of 20 and 50 Torr. These differ from the records of single spin in unsupported detonations, however, in that the fine structure found within the transverse wave band in the latter records[2,6] is absent. Foils placed only on the end wall are more durable and are generally easier to work with. These record the location of radially or circumferentially propagating creases in the shock front anywhere in the tube cross section upon arrival of the wave at the end. Single spinning waves are recognized by the presence of a single, more or less radially oriented mark extending inward from the rim.[2]

Another prominent characteristic of single spinning waves is severe departure of the shock front from planarity.[2,6,7] This leads to scatter in the apparent shock wave velocity deduced from the time intervals between arrival of the shock at gauges spaced arbitrarily along the tube. This scatter in apparent velocity was observed to be as great as $\pm 10\%$ over 30 cm intervals in waves where the end foils revealed the presence of single spin. That this scatter is in fact attributable to the revolving, nonplanar shock front which moves at much more nearly constant average axial velocity is confirmed by the differences in arrival times measured by the four pressure gauges placed in a ring around the tube. These differences were as great as 11 μsec, corresponding to a 15 mm differential in axial position, in shock waves where the smoked foil confirmed the presence of single-headed spin.

Finally, the occurrence of single-headed spin is demonstrated very graphically in the open shutter photograph reproduced in Fig. 1.

Quantitative examination of the conditions under which spin and related instability phenomena occur is hampered by the uncertainty in the measurement of the axial velocity with the present interval method. Nevertheless, determination of the approximate ranges of conditions under which spin is observed has been pursued. The Chapman-Jouguet velocity of the 1% C_2H_2, 1.5% O_2, 97.5% Ar mixture initially at room temperature and ca. 0.1 atm pressure is about 0.9 km/sec, and the velocities of the shock waves studied were between 1.0 and 2.0 km/sec. At each of the three initial pressures studied, there is a range of shock velocities above 1.0 km/sec in which neither single-headed spin nor any other discernible perturbation at the shock wave front was observed. At p_0 = 20 and 50 Torr, the occurrence of chemical reaction behind the shock front was indicated at shock velocities above ca. 1.1 km/sec by the growth and subsequent leveling off of absorption of the ultraviolet line radiation of OH. But evidence of spin was not present in smoked foil or open shutter photographic records except at velocities above ca. 1.2 km/sec for p_0 = 50 Torr and above ca. 1.33 km/sec for p_0 = 20 Torr. At 120 Torr, single-headed spin occurred at velocities as low as ca. 1.10 km/sec, but not at still lower velocities. At these lower velocities, where for normal shock waves the temperature before reaction lies below about 1300°K, OH radical absorption did not provide a good means of detecting the occurrence of reaction, even though other work[9] has shown that the induction zone, scaled for density of reactants, lies well within the time and space regimes of the present experiments. Evidently, little OH is formed unless the combustion takes place at higher temperatures than this.

When the shock velocity was raised above the threshold range for single spin, spin modes of higher multiplicity were obtained. For example, at p_0 = 50 Torr, single-headed spin was obtained fairly reproducibly near 1.3 km/sec, but shock fronts with 2, 3, or 4 visible creases extending to the perimeter of the end plate smoked foils were common near 1.4 km/sec. The ability of smoked and plate foils to record the impingement of highly segmented fronts in the interior of the shock tube, as has been done so successfully in unsupported detonations,[2,10] was disappointing. At shock velocities above ca. 1.5 km/sec at p_0 = 50 Torr, only small, isolated segments of wave intersection tracks were recorded. Thus while the presence of persistent spin-like perturbations is indicated, it was not possible to observe any orderly structure or study variation of structure with shock velocity.

OH absorption oscillograms showed pronounced undulations not only in experiments where single spin was indicated, but also in experiments with coarse multiheaded spin. In still faster shock waves, though, the structure was evidently of sufficiently fine scale and/or low intensity that properties averaged over the tube diameter, as by a photon beam absorption experiment, may become usable for determination of combustion stoichiometry and the course of slow chemical changes that follow behind the induction zone.

Another regime of interesting phenomena was found in reactive shocks at velocities just below those at which single-headed spin was observed. OH absorption oscillograms were not reproducible, sometimes indicating abrupt formation of large quantities of OH and on other occasions, under closely similar conditions, showing scarcely detectable appearance of OH. Raster oscilloscope records of the shock wave progress down the tube showed scatter which was appreciable, with differences in apparent velocity as large as 3% between successive 30 cm intervals. Tests revealed corresponding departures of the shock fronts from planarity, which were only about one-third as large as those found when spin was identifiable. Smoked foil records showed no creases extending to the perimeter of the tube. Instead, end plate foils showed patches of indistinct disturbance in the interior of the tube.

On the basis of this somewhat incomplete characterization of these subspinning instabilities, it is hypothesized that they represent irregularities in the reaction zone which are not of sufficient, localized exothermicity to extend their influence in large amplitude form to the shock front or are not of proper wavelength to couple to acoustic oscillations of the burned gas. Attention is here drawn to interferograms of reactive shock waves in dilute exothermic systems, including an NH_3 - O_2 system[11] and one of the H_2 - O_2 - Ar mixtures[12] previously used for kinetics studies in our Laboratory[5] in which at initial pressures between 100 and 200 Torr there had been pronounced undulations in OH absorption oscillograms. These interferograms showed that the shock front is quite flat, though slightly tilted in the tube, but the reaction zone is much more significantly disturbed. It also seems appropriate to report that attempts to record smoked foil inscriptions in the H_2 - O_2 - Ar mixture under these same conditions gave negative results.

To relate the present work in acetylene - oxygen mixtures to other work in the same system, we note that most of the kinetics studies,[13] some of which have used more concentrated mixtures than the present one, have been done in an initial pressure regime an order of magnitude lower. In addition, many of the studies have been done using reflected shock waves and in ways which are not so subject to interference by transverse waves either at the shock front or in the reaction zone.

The occurrence of spin in an environment divorced from marginally propagating detonation would appear to offer a heretofore unrealized opportunity to study the limiting conditions for the occurrence of spin with additional variables at one's command in the hope of elucidating detonation limit phenomena. The lack of sharpness of the limits observed in the present system detracts somewhat from the attractiveness of this approach, but further work may be appropriate.

A brief attempt is made here to relate some parameters of the single spinning waves observed in these driven shock waves to known properties of the chemical mixture. From the admittedly approximate values of the threshold velocities for spin, $D_{threshold}$, at the three experimental initial pressures, the induction times t_i and axial induction zone lengths x_i for the temperature and density behind the axially normal portions of the convex spinning shock fronts have been evaluated from independent induction period data.[9] These values are recorded in Table I, where it can be seen that the induction zone lengths for these spinning waves are not constant, but become smaller at lower density, and are all smaller than the 100 mm tube diameter.

The mean pitch angle, Θ, from smoked side foils and the mean axial velocity, D, were obtained from separate experiments, done for p_0 = 20 and 50 Torr, each at constant tube loading conditions. These data were combined to determine the circumferential velocity component of the single spin under these two conditions. In Table II these are recorded and compared with the perimetral velocity for pure fundamental circumferential oscillation in the reacted gas estimated for a plane shock wave at the axial velocity D with reaction to chemical equilibrium (1.84 times the sound velocity, c).[14] Also tabulated are the Chapman-Jouguet detonation velocities D'_{CJ} for the unsupported detonation of the hot, compressed, unreacted gas behind the primary shock front having velocity D. The circumferential velocity of the transverse spin wave at the tube perimeter is seen to lie between these two characteristic velocities of the system, which are sufficiently different from each other under the present experimental circumstances that the spinning wave cannot be in close resonance with both, as it has been found to be in certain unsupported spinning detonations.[14,15]

In simplest terms, the experiments described here show that the occurrence of single-headed spin, which may be universally associated with unsupported detonations at the limits of their ability to propagate, is not exclusively a property of unsupported waves or of Chapman-Jouguet flow.

The initial experiments in which the occurrence of spin in this acetylene - oxygen - argon mixture was first identified were carried out in July 1963 by M. P. Eastman and P. F. Bird, and in collaboration with Prof. R. A. Strehlow. J. L. Young and J. G. Williamson carried out most of the subsequent experimental work.

Table I. Normal Shock Induction Zones at Spin Threshold for 1% C_2H_2, 1.5% O_2, 97.5% Ar in 10 cm diameter tube.

p_0	$D_{threshold}$	T	t_i	x_i
Torr	km/sec	°K	μsec	mm
20	1.33	1820	52	20
50	1.20	1518	83	29
120	1.10	1317	122	41

Table II. Circumferential Velocity Considerations for Single-Headed Spins in Driven Shock Waves.

p_0	D	Θ	1.84 c	D cotΘ	D'_{CJ}
Torr	km/sec		km/sec	km/sec	km/sec
20	1.38	46°	1.59	1.33	1.25
50	1.31	43°	1.53	1.40	1.24

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Figure 1.

Still photograph of luminosity of driven shock, D = 1.3 mm/μsec, in 1.0% C_2H_2, 1.5% O_2, 97.5% Ar at 50 torr. in 10 cm diameter glass tube. Shock motion left to right.